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THERMALLY-INDUCED STRUCTURAL CHANGES IN COPPER-CONTAINING CHALCOGENIDE THIN FILMS

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Thin-film samples of the system $Cu_x(AsSe_{1.4}I_{0.2})_{1-x}$, x<15 at%, were prepared by the method of thermal evaporation on "cold" substrates in vacuum, using a specially constructed quartz cell as evaporation chamber. The method of transmission electron microscopy was employed to follow the structural changes taking place in the course of thermal treatment of the freshly deposited film samples. It was found that the contents of selenium and copper in the starting glass have a decisive role in determining the structure and properties of the material. The observed microgranular two-phase structures of thin films have a grain size of the order of 10 nm. Heating of the samples to the softening temperature yields the structural transformation in the films from the starting amorphous phase to a new amorphous phase. Also, the temperatures were determined at which partial crystallization takes place, resulting in the separation of crystalline centers of the elemental selenium.

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1. Introduction

In the last decades, thin films of various compositions have become the materials of significant practical applications. Thus, it has been shown that their excellent characteristics are of technological importance, for example in manufacturing cathode tubes and microelectronic circuits. On the other hand, they found equally important application in the industry where they are used as the elements of mass-products as transparent coatings on plastics and textile or sunglasses, for example.

It has been shown that samples of chalcogenide amorphous materials can be relatively easily obtained in the form of thin films, whereby all relevant desirable characteristics of these amorphous systems are preserved. It should be especially pointed out that the photo-induced changes of properties in the chalcogenide glasses could appear even in the absence of classical photochrome components in their composition [1, 2]. Most probably, relatively low energies of the chemical bonds in these structures can ensure the occurrence of photochemical reactions and photo-structural transformations. This holds even for photo-crystallization. All these facts are of invaluable importance for the application of thin films of chalcogenide systems as a medium for information recording that can be erased by thermal annealing at a temperature below the softening point [3]. In view of the fact that optical recording is based on the change of the absorption coefficient of electromagnetic radiation and the coefficient of refraction, primarily as a consequence of structural transformations *amorphous phase* $\Leftrightarrow$ *crystal, amorphous* $\Leftrightarrow$ *amorphous* or, possibly, because of the change of magnetic polarizability, one of the primary tasks is to resolve the question of the mechanism of information recording and erasing. In this work we present the results obtained in a study of the effect of temperature on the structural properties of thin films from the system Cu-As-Se-I.

2. Experimental

Thin-film samples of the $Cu_x(AsSe_{1.4}I_{0.2})_{1-x}$ system were obtained by thermal evaporation and condensation in vacuum of the priorily synthesized glass of the given composition. Because of the

complex composition of the starting glass use was made of a special quartz cell as the evaporation chamber allowing the discrete evaporation at optimal temperatures [4]. The glass was synthesized by the previously described procedure of cascade heating and annealing in air [5]. The films were deposited on the glass plates of the known refraction index, kept at room temperature. The film thickness in the process of vapour-deposition was controlled by optical method based on the interference of the reflected laser beam and it was 1.08, 1.22 and 0.77 mm for the samples with 0, 5 and 15 at.%, respectively, which enabled investigation of the films by the method of transmission electron microscopy (TEM) [6]. The film structure was investigated using an electronic microscope EMV-100B additionally equipped with a camera for electron diffraction of the type EMR-100. The character of the structural transformations taking place in the films with increase in temperature were studied by monitoring the changes resulting from the heating of the freshly-prepared samples from room temperature to 200 °C at a rate of 0.5 °/s.

3. Results and discussion

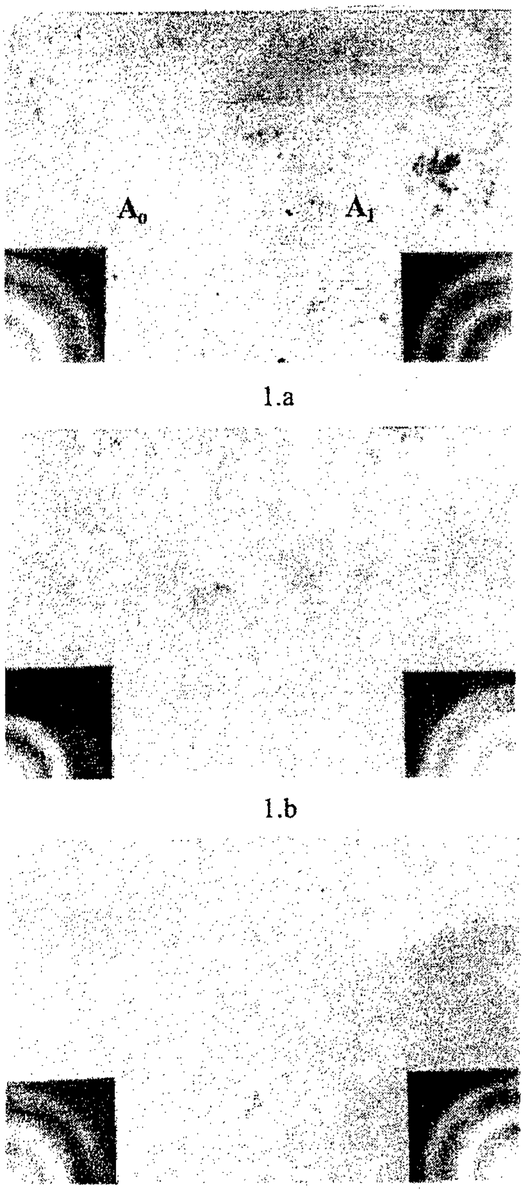
Mass spectrometry was used to control the relative composition of the vapour in the process of thin-film preparation. It was found that the mass spectra are characterized by those structural units that enter the composition of the corresponding glass. In Figs. 1.a–1.c are presented the TEM photographs of freshly prepared films of the investigated chalcogenide system. The photographs (magnification 40,000) were taken for a sample containing no copper and the samples with 5 and 15 at.% Cu. Figs. 2a–2c illustrate the changes caused by thermal treatment of the same samples.

In the same figures are shown the photographs of electronic diffraction patterns taken for each of the observed situations. As can be seen, electronic microscopy showed that freshly deposited films of the ternary glass $AsSe_{1.4}I_{0.2}$ has a microgranular structure, whereby the grain size is of the order of magnitude of 10 nm. Over the whole film surface there are randomly distributed irregular amorphous forms of Se (Fig. 1a).

In the course of heating to the softening temperature, some structural changes take place in the film from the starting amorphous phase to a new, also amorphous phase (in the figure designated as A0 → A1). At about 105 °C crystallization of Se on the film surface takes place (this is confirmed by the crystalline forms present on the sites of the amorphous ones), as well as in the film itself, which is visible as dark grains over the whole picture (Fig. 2a). Further increase in temperature (to the softening point) yielded no significant changes in the film structure.

The freshly deposited films of the composition $Cu_5(AsSe_{1.4}I_{0.2})_{95}$ have a structure very similar to that obtained for the ternary samples (Fig. 1b). It is also possible to observe the structural change A0 → A1, whereby the amorphous character has been preserved. At a somewhat different temperature (Tt ~ 110 °C) Se crystallization in the film takes place, but the dominant character of crystallization differs from the corresponding process observed with the sample containing no copper. Namely, in this case, the process of Se separation and crystallization is dominant in the whole thin-film volume, which confirms the formation of a more distinct grainy structure and uniform increase in the size of dark spots over the whole picture (Fig. 2b).

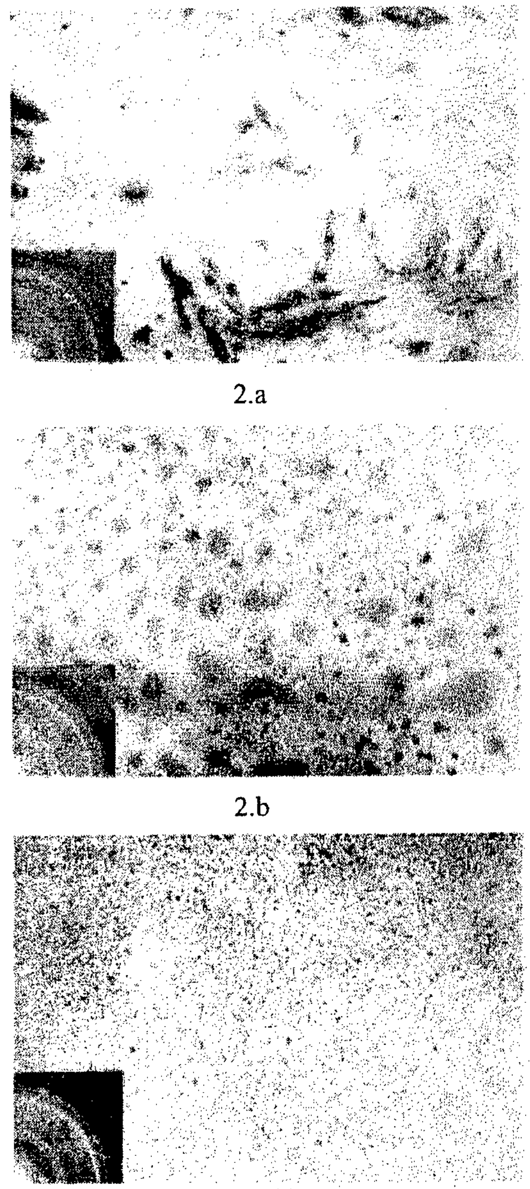
The film $Cu_{15}(AsSe_{1.4}I_{0.2})_{85}$ is essentially different, still in the initial phase. Namely, the microgranular structure is more clearly formed in which there is no Se on the surface (Fig. 1c). Analogously to the other samples, the transition A0 → A1 (motion of the dark front in the microscope field of vision) is observed, and the heating (Tt ~ 125 °C) yields crystallization of selenium, which is evident from the forms characteristic of its crystalline state (Fig. 2c).



1.a

1.b

1.c



2.a

2.b

2.c

Fig. 1. TEM micrograph and x-ray diffractogram of as-evaporated thin films:
a – $AsSe_{1.4}I_{0.2}$;
b – $Cu_5(AsSe_{1.4}I_{0.2})_{95}$;
c – $Cu_{15}(AsSe_{1.4}I_{0.2})_{85}$.

Fig. 2. TEM micrograph and x-ray diffractogram of thermally annealed films:
a – $AsSe_{1.4}I_{0.2}$;
b – $Cu_5(AsSe_{1.4}I_{0.2})_{95}$;
c – $Cu_{15}(AsSe_{1.4}I_{0.2})_{85}$.

The identification of two different amorphous phases, that is the corroboration of their existence, is of special importance for the interpretation of photorecording phenomena. It is important to point out that the values of transformation temperatures are in excellent agreement with the softening temperature of the non-crystalline material of the corresponding composition vapour-deposited on a cold substrate, determined by other experimental methods [7,8].

4. Conclusions

The detected changes give the ground to the conclusion that the structure and properties of the films of the Cu-As-Se-I system are mainly determined by the contents of Se and Cu in the starting

glass. It is obvious that lower contents of Se in the sample yield also lower population of individual centres on the film surface, and thus result in a more homogeneous film. This causes the difference in the mode of Se crystallization in the samples of different compositions. On the other hand, the increase in Cu content in the starting glass obviously yields to the increase in the population of the centres that induce structural transformations and crystallization (the temperature of Se crystallization decreases with increase in Cu content of the sample).

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